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Nitrogen-doped carbon-coated MnO nanoparticles anchored on interconnected graphene ribbons for high-performance lithium-ion batteries

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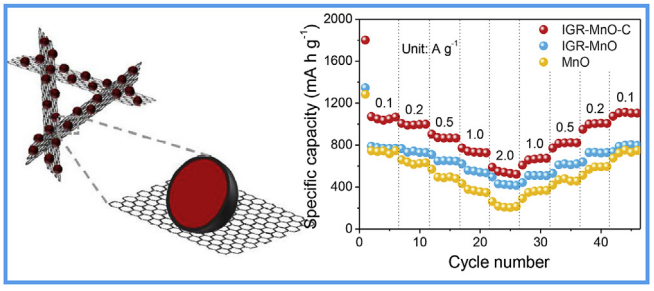
HIGHLIGHTS

- N-doped carbon-coated MnO anchored on graphene ribbons (IGR-MnO-C) are designed.
- IGR-MnO-C possesses high electrical conductivity and structural integrity.
- IGR-MnO-C shows high capacity and excellent rate performance.

GRAPHICAL ABSTRACT



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ABSTRACT

The construction of the anode materials with high-rate and long-life performance for lithium-ion batteries (LIBs) still remains a great challenge due to their poor electronic conductivity and drastic volume changes during the lithiation and delithiation processes. Herein, we report nitrogen-doped carbon-coated MnO nanoparticles anchored on the interconnected graphene ribbons (IGR-MnO-C) as a anode for LIBs. As a result, the IGR-MnO-C exhibits a high reversible capacity (1055 mAh g^{-1} at 0.1 A g^{-1}), excellent rate capability (547 mAh g^{-1} at 2 A g^{-1}) and stable cycling performance (550 cycles with 113% capacity retention at 0.5 A g^{-1}). The strategy proposed in this work can be further extended to other transition metal oxides for the applications in supercapacitors, sodium-ion batteries and fuel cell.

1. Introduction

The rapid development of portable electronic devices and hybrid electric vehicles markets has spurred internationally unprecedented interest in exploring high-energy energy storage devices for electric power. Among them, lithium ion batteries (LIBs) have gained considerable research attention over the past several years because of their relatively high energy density and cyclability [1–7]. But practically, their performance still cannot meet the requirements of current applications, and is expected to be further upgraded [8]. It is well-accepted that the overall performance of LIBs greatly depends on the electrode materials [9]. Throughout the past decades, graphite or hard

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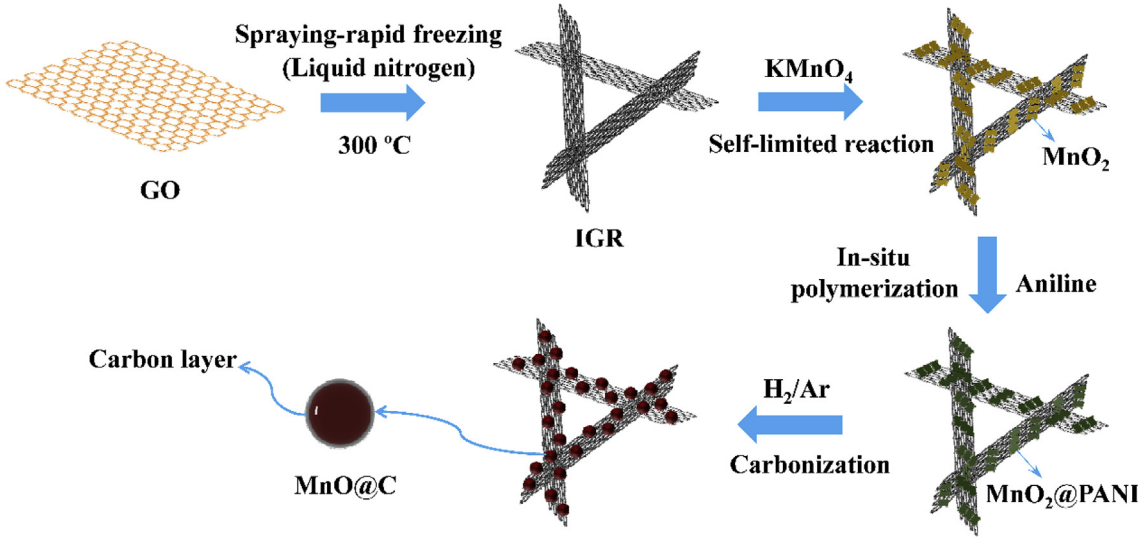

Scheme 1. Schematic illustration of the fabrication of IGR-MnO-C.

carbon is the most commonly used anode active materials in LIBs [10]. However, their application in high-energy-density LIBs is seriously affected by the limited theoretical capacity (with a value of 372 mAh g^{-1} for graphite) based on the classical Li insertion/deinsertion mechanism [11]. Thus, much effort has been devoted to the investigation of other anode materials for LIBs in order to achieve the enhanced lithium-ion storage capacity. Transition metal oxides (TMOs, where M represents Co, Ni, Mn or Fe) represent potential alternatives to traditional carbonaceous materials due to higher theoretical specific capacities [12–15]. Among those TMOs materials, manganese oxide (MnO) has drawn lots of attention because it has some merits such as low conversion potential, relatively high theoretical capacity (756 mAh g^{-1}), low cost, abundant resource of Mn, environmental friendliness, and so forth [16,17]. Unfortunately, MnO faces the major issues such as intrinsically poor electronic conductivity and significant volume expansion (> 170%) during the charge/discharge process, typically resulting in inferior rate capability and poor cycle life [16]. Nowadays, the hybridization of MnO with electrochemically stable and highly conductive materials is considered as a promising and effective strategy [18–24], however, the improvements of rate capability and cycling performance are still needed for practical application [19,21]. Therefore, a rational design of MnO-based anode materials with high electrical conductivity and structural integrity is extremely desirable.

Graphene ribbons have high length-to-width ratio, a large amount of edges with high electron density, and quasi-one dimension, which makes them less prone to aggregation [25,26]. Consequently, graphene ribbons seem to be an ideal carbon matrix for supporting transition metal oxides as electrode materials for energy storage. To the best of our knowledge, anchoring metal oxide onto graphene ribbons is rarely reported. Additionally, currently available fabrication techniques of graphene ribbons mainly are longitudinal unzipping of carbon nanotubes and chemical vapor deposition [26]. Therefore, it is necessary to further develop a novel and efficient strategy for the preparation of graphene ribbons.

Recently, our group has reported a feasible route for easy preparation of interconnected graphene oxide ribbons (IGOR) by a "spraying-rapid freezing" process [27,28]. Herein, we report a facile and effective method to synthesize nitrogen-doped carbon-coated MnO anchored on interconnected graphene ribbons (denoted as IGR-MnO-C). MnO nanoparticles are tightly coated by polyaniline-derived nitrogen-doped carbon, and meanwhile closely anchored on the interconnected graphene ribbons network, ensuring both high electrical conductivity and structural integrity of the electrode. As the anode materials for LIBs, the IGR-MnO-C exhibits a high reversible capacity (1055 mAh g^{-1} at 0.1 A g^{-1}), excellent rate performance (547 mAh g^{-1} at 2 A g^{-1}) and cyclic stability (550 cycles without capacity loss).

2. Experimental

2.1. Preparation of IGR

Graphene oxide (GO) was initially obtained from natural graphite according to a modified Hummers' method [29], and then used as the starting materials for fabricating interconnected graphene ribbons (IGR). For the synthesis of IGR, a certain amount of GO aqueous dispersion (1.0 mg mL^{-1}) in a sprayer was sprayed into a liquid nitrogen bath in the form of the tiny droplet, and then the rapidly-frozen ice particles was subjected to lyophilization process followed by annealing at 300 °C for 2 h in nitrogen flow.

2.2. Preparation of IGR-MnO_2

For the synthesis of IGR-MnO_2, 40 mg as-prepared IGR were dispersed in 100 mL deionized water with ultrasonication for 10 min. And then, 291 mg $KMnO_4$ was added into above suspension. After being stirred at room temperature for 30 min, the mixture was transferred into a microwave reactor (700W) to react for 7 min. After the reaction, the product was collected by filtration, washed with water, and lyophilized.

2.3. Preparation of IGR-MnO-C and IGR-MnO

In a typical synthesis of IGR-MnO-C, 100 mg as-obtained IGR-MnO_2 was uniformly dispersed in 30 ml of deionized water. In the meanwhile, 15 μL of aniline monomers were added into a proper amount of 0.5 mol L^{-1} H_2SO_4 solution. After that, the aniline monomer-contained H_2SO_4 solution and IGR-MnO_2 dispersion were mixed together to polymerize for 2 h. The resultant dark-green product was washed with alcohol and deionized water for several times, and freeze-dried. Finally, the IGR-MnO_2-PANI was thermally treated at 800 °C under H_2/Ar gas